

Photoinduced processes in chromophore–gold nanoparticle assemblies*

Anne Kotiaho[‡], Riikka Lahtinen, and Helge Lemmetyinen

*Department of Chemistry and Bioengineering, Tampere University of Technology,
P.O. Box 541, 33101 Tampere, Finland*

Abstract: Development of nanotechnology requires that the interaction between components of nanoscale devices can be studied and understood better. Photoinduced processes between small (2–5 nm in core diameter) gold nanoparticles (GNPs) and chromophores, including porphyrin, fullerene, and phthalocyanine, were studied. Two methods were selected for controlled assembly of chromophores and gold particles at close distances: thin films and covalent attachment, which yields chromophore-functionalized particles. Time-resolved spectroscopic and photoelectrical measurements carried out further confirmed the known strong effect of GNPs on photoexcited chromophores that leads to fast photoinduced processes. When GNPs are combined with suitable chromophores, the particles can act as electron donors or acceptors. GNPs are efficient energy acceptors, and some indications of their ability to act as energy donors were obtained. The participation of the GNPs in photoinduced charge transfer in addition to energy-transfer processes makes them attractive components for photoactive devices.

Keywords: electron transfer; energy transfer; fluorescence; gold nanoparticles; phthalocyanines; porphyrins.

INTRODUCTION

There are several known interaction mechanisms for chromophores and close-by gold nanoparticles (GNPs). In a number of cases, fluorescence of an adjacent chromophore is quenched by GNPs due to energy or electron transfer [1]. Quenching usually takes place if the particles are small and the distance between the chromophore and the particle is short. In some cases, the radiative lifetime of the chromophore has been reported to alter in chromophore–GNP assemblies [2], which can, in optimal conditions and sufficient size (>40 nm) of the GNPs, lead to fluorescence enhancement [3,4].

The present paper focuses on our research on photoinduced processes in chromophore–GNP assemblies with a connection to selected literature references. We used two strategies in assembling GNPs and chromophores at close distances: thin film preparation and covalent attachment in chromophore-functionalized GNPs. In the first approach, monomolecular, organized films were prepared by Langmuir–Blodgett or –Schäfer methods. A monolayer of the chosen chromophore was deposited on a substrate, usually a glass plate, followed by deposition of a layer of octanethiol-protected GNPs. The chromophore and GNP layers can be deposited in different order, and multilayer deposition is also possible when thicker films are required. In the second approach, chromophore-functionalized GNPs were

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[‡]Corresponding author: Present address: Laboratory of Fibre and Cellulose Technology, Åbo Akademi University, Porthansgatan 3, 20500 Åbo, Finland; E-mail: anne.kotiaho@abo.fi

prepared by a ligand-exchange reaction, where the particles have initially a tetraoctylammonium bromide protecting layer which is partially exchanged to chromophores having thioacetate-terminated linkers. The porphyrin- and phthalocyanine-functionalized GNPs were studied in toluene solutions. The particles used were relatively small; the core diameter for particles studied in films was 2–3 nm and 5 nm for the chromophore-functionalized particles. By using different tools of optical spectroscopy, for example, time-resolved fluorescence and absorption methods and photoelectrical measurements, it was possible to observe a number of photoinduced processes taking place both in the thin films and in the chromophore-functionalized GNPs (Fig. 1).

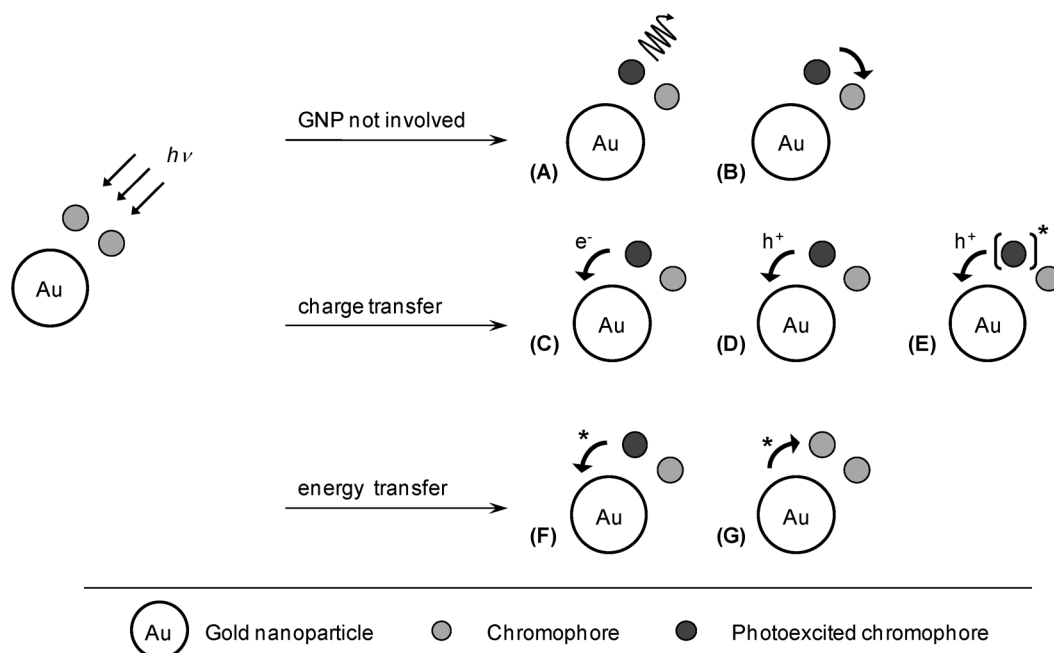


Fig. 1 Possible photoinduced processes in chromophore–GNP assemblies: (A) unquenched fluorescence, (B) interchromophore interactions, (C,D) electron (or hole) transfer from a photoexcited chromophore to a GNP, (E) formation of an intramolecular excited state in a chromophore followed by charge transfer to a GNP, (F) energy transfer from a chromophore to a GNP, and (G) energy transfer from a photoexcited GNP to a chromophore.

CHARGE TRANSFER IN FILMS

Cases where charge transfer from photoexcited chromophores to GNPs is reported are far less than those related to energy transfer. The first case, where photoinduced electron transfer was reported, considered pyrene-functionalized GNPs [5]. Electron transfer from pyrene to gold cores was observed to take place when short linkers (2–8 atoms) were used and to be favored in polar solvents [6]. Electron transfer was also demonstrated from electrostatically assembled chlorophyll molecules to GNPs [7]. Recently, photoinduced electron transfer from GNPs to perylene diimide was proposed in perylene diimide–GNP hybrids [8].

Photocurrent is a direct way to measure charges, while charge transfer is manifested by appearance of photoinduced absorption bands of radical anions or cations in time-resolved absorption measurements. In the case of the GNPs, it seems reasonable to assume that the addition or removal of one electron will not create significant changes in the absorption spectrum. One method of studying charge transfer in films is time-resolved Maxwell displacement charge technique [9,10]. This method is very

sensitive and nondestructive. The photoactive layers are insulated from electrodes, and the photo-induced charge movement perpendicular to electrode surfaces induces a voltage, which can be measured as a function of time. The sign of the signal indicates the direction of charge movement, the amplitude is proportional to the charge separation distance and number of separated charges, and the decay of the photovoltage signal is caused by charge recombination.

An indication of the ability of GNPs to act both as electron acceptors and donors to photoexcited chromophores was obtained from photovoltage measurements of simple bilayer films. The GNP layer was combined with monolayers of a porphyrin derivative, a fullerene derivative, and a conducting polymer, polyhexylthiophene (PHT). The photovoltage signals indicated electron transfer from the particles to porphyrin or fullerene [11] and electron transfer from PHT to the particles [12]. From these bilayer structures, the one with porphyrins and GNPs was chosen for more detailed studies. A clear indication of charge transfer is obtained by reversing the order of deposition of the two layers, and observing a change in the sign of the photovoltage signal. This is shown for porphyrin|GNP bilayers in Fig. 2A. The signals indicate electron transfer from GNPs to porphyrins [13].

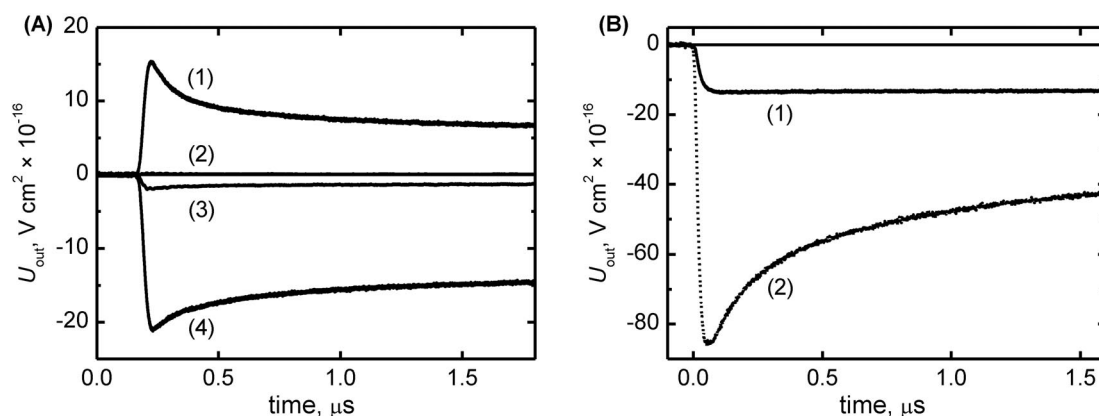


Fig. 2 Photovoltage decays for (A) films containing porphyrins and GNPs: substrate|porphyrin|GNP (1), substrate|GNP|porphyrin (4), substrate|GNP (2), and substrate|porphyrin (3) and (B) for films containing porphyrin-fullerene dyads and GNPs: substrate|porphyrin-fullerene (1) and substrate|GNP|porphyrin-fullerene (2). Excitation wavelengths were 422 and 430 nm, respectively.

Since promising photovoltage signals were observed for porphyrin|GNP films, the GNPs were combined with films of porphyrin-fullerene dyads (see Fig. 3A for a dyad structure). Porphyrin-fullerene dyads are known to perform fast and efficient intramolecular electron transfer as a result of photoexcitation of the porphyrin moiety [14–16]. The charge-separated state is reached via an exciplex intermediate state [17]. Dyad molecules with hydrophilic groups are able to organize at the air–water interface, allowing deposition of monolayers, where photoinduced, vectorial electron transfer takes place between the porphyrin and fullerene planes [18]. The electron transfer of such a porphyrin-fullerene monolayer is enhanced by a GNP monolayer deposited adjacent to the porphyrin moieties [11,19], as shown in Fig. 2B. This is the highest photovoltage observed for GNP-containing film structures. More detailed analysis of the photovoltage results indicates that creation of the photovoltage requires excitation of the dyad [11]. A possible scheme for charge transfer would be intramolecular charge separation of the dyad followed by hole transfer from the porphyrin to the GNPs. Measurements of fluorescence spectra and lifetime indicate that the exciplex emission of the dyad is partially quenched by the particles [19]. As the exciplex formation is fast (<0.5 ps [20]) and takes place intramolecularly,

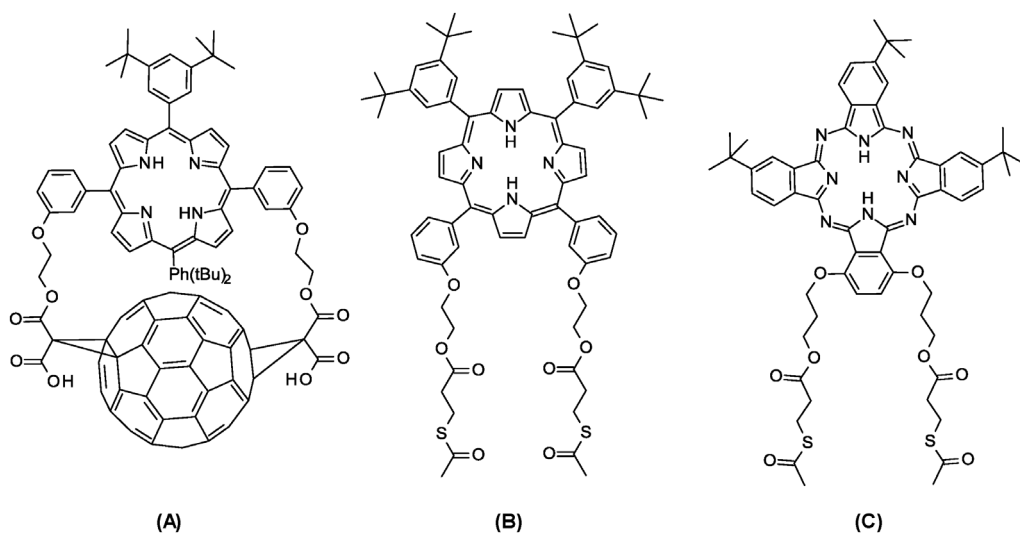


Fig. 3 Chemical structures of (A) porphyrin-fullerene dyad and (B,C) porphyrin and phthalocyanine with linkers for attachment to GNP surface.

the quenching of the exciplex cannot be due to prevention of its formation by the GNPs but rather due to faster relaxation of the exciplex either to ground state or charge-separated state.

The photovoltage measurements of films indicate charge transfer, but the downside of the photovoltage measurements is the difficulty of estimating charge transfer efficiency accurately. As GNPs are known to be efficient energy acceptors, the relative importance of charge transfer and energy transfer was studied using porphyrin|GNP bilayer films. Porphyrin films were chosen because of relatively easy film preparation and distinct absorption and fluorescence properties.

ENERGY TRANSFER IN FILMS

Energy transfer from photoexcited chromophores to GNPs is by far the most studied process in chromophore-functionalized GNPs. Different types of fluorescent compounds, including small dyes [21–24], conjugated polymers [25], semiconductor quantum dots [26], and large molecules such as porphyrin [27] and fullerene [28] show quenching of fluorescence on GNP surfaces due to energy transfer.

The two traditional mechanisms used to explain energy transfer are Dexter- and Förster-type energy transfers [29]. The Dexter mechanism (electron exchange) is of short range (<1 nm) and requires overlap of molecular orbitals. The Förster resonance energy transfer (FRET) is dependent on the sixth inverse power of distance for two interacting point dipoles. The Förster radius or critical distance of energy transfer is determined by spectral overlap of donor fluorescence and acceptor absorption, relative orientation of the molecular dipoles and fluorescence quantum yield of the donor. In the case of systems containing GNPs, the Förster mechanism seems not to be fully valid, because the range of Förster energy transfer has been exceeded in these systems. A more appropriate mechanism is considered to be nanometal surface energy transfer (NSET) (see ref. [30] and the refs. therein). Comparing to Förster mechanism, NSET produces similar distance dependence as FRET between a layer and point dipole: fourth inverse power of distance. The most profound difference comes from the factors affecting the critical distance, which are donor quantum yield, frequency of donor electronic transition, Fermi frequency and wave vector of the metal in the case of NSET. In NSET, electromagnetic field of the donor dipole interacts with the conduction electrons of the metal, and therefore resonant electronic transition is not needed.

As mentioned earlier, the relative importances of the charge and energy transfers were estimated for porphyrin|GNP films [13], where the fluorescence of porphyrin is strongly quenched. Time-resolved absorption measurements, performed with a pump–probe set-up, of a porphyrin film show two components which are both ascribed to the first excited singlet state (Fig. 4A). For GNPs, excitation with a laser pulse increases the temperature of the electrons. The excess energy is distributed among all the electrons via electron–electron scattering and the electrons cool further to the lattice temperature by electron–phonon scattering and finally the particles release heat to the surrounding media by phonon–phonon scattering [31]. The 2 ps component observed for GNP film in pump–probe measurements corresponds to electron–phonon scattering (Fig. 4A).

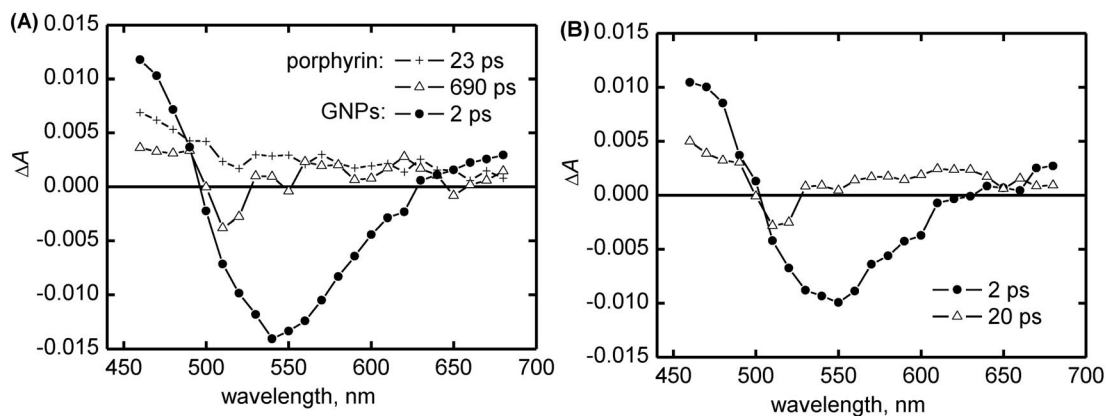


Fig. 4 Decay component spectra obtained from global fitting of pump–probe data for (A) porphyrin and GNP films (B) porphyrin|GNP films. Excitation wavelength was 420 nm. Reprinted in part with permission from *J. Phys. Chem. C* **112**, 20316 (2008). Copyright © 2008 American Chemical Society.

In the porphyrin|GNP film, the lifetime of the porphyrin first excited singlet state is reduced significantly (Fig. 4B). Though the photovoltage signal indicates charge transfer, no evidence of charge transfer was found in the form of photoinduced absorption bands of porphyrin radical anions from time-resolved absorption measurements. This indicates energy transfer in 20 ps from the porphyrin film to the GNP film. From flash photolysis measurements, it is possible to say that absorption of the triplet state in porphyrin|GNP film is 10 % compared to the porphyrin film. The lower limit of charge transfer efficiency is calculated from photovoltage measurements to be 0.3 %. The upper limit is estimated to be <10 % based on flash photolysis results, taking into account the absorption coefficient of porphyrin radical anion and the noise level of the instrument. This is to say that the charge separation efficiency is too low for the radical anion band to be visible by time-resolved absorption measurements. In conclusion, the porphyrin molecules relax mainly via energy transfer from the first singlet excited state.

As the main relaxation pathway of porphyrins adjacent to the GNP layer was concluded to be energy transfer, the distance dependence of fluorescence quenching was studied [13]. This was done by placing spacer layers between porphyrin and GNP films. The energy transfer efficiency is inversely proportional to the second power of distance, indicating energy transfer between layers.

PORPHYRIN- AND PHTHALOCYANINE-FUNCTIONALIZED GNPs

The studies on porphyrin|GNP films indicated efficient energy transfer. Imahori et al. have studied in detail porphyrin-functionalized GNPs, and concluded energy transfer to take place [27,32]. In our studies, two porphyrin derivatives with linkers at different positions of the porphyrin molecule were pre-

pared [33] (see Fig. 3B for one structure). Two linkers are probably enough to allow firm attachment of the porphyrins to particle surface, but the optimum set-up for controlling the attachment would be one rigid linker for vertical orientation and four rigid linkers for horizontal orientation. However, even a difference in position of the two linkers was enough to cause differences in stability of the particles and minor differences in fluorescence lifetimes [33]. The energy transfer in films takes place in ~ 20 ps, and is even faster in porphyrin-functionalized GNPs according to fluorescence up-conversion measurements [33]. The fluorescence lifetimes of the porphyrins attached to GNPs are 3–5 ps.

The same synthetic approach used with preparation of porphyrin-functionalized GNPs could be applied to phthalocyanine-functionalized GNPs [34] (see Fig. 3C for the phthalocyanine structure). The phthalocyanine molecules are closely packed on the particle surface and some broadening of the phthalocyanine Soret-band around 340 nm and significant broadening of the Q-bands at 700 nm are observed in absorption spectrum. The fluorescence of the phthalocyanines is strongly quenched after attachment to GNPs. Even though the phthalocyanine-functionalized GNPs were purified carefully from free phthalocyanines using size-exclusion chromatography, there are some phthalocyanine molecules that have fluorescence properties similar to ones free in solution. This is either a result of small amount of free phthalocyanines surviving the purification step, or more likely, due to minor detachment of phthalocyanines from the surface of the particles. To find out the exact reason for the fluorescence quenching in phthalocyanine-functionalized GNPs, pump–probe measurements were performed.

An important factor to be considered while performing pump–probe measurements of GNPs is the dependency of the relaxation lifetimes on excitation energy density. In our case, this was taken into account by having similar absorptions of GNPs for any samples to be compared, and by measuring the samples successively on the same day to exclude any variations in laser power. The pump–probe measurements show phthalocyanine Q-band bleach and reduction of the component lifetime of the GNPs after nearly selective excitation of the gold cores (Fig. 5A). The attachment of phthalocyanine molecules on the particle surface leads to broadening of absorption bands, and thus some phthalocyanine molecules are directly excited in the phthalocyanine-functionalized GNPs, even if the absorption coefficient of the free phthalocyanines in solution is very low at 500 nm. According to a rough estimation, this direct excitation should result in a lower amplitude of the bleach than what is actually observed. The appearance of the phthalocyanine bleach can also be interpreted as an indication of energy transfer from the gold cores to the phthalocyanines. Some further studies are required to fully confirm the role of GNPs as energy donors. The photoexcited, oscillating electrons in GNPs lose their coherence fast, in about 50 fs [35], and any energy-transfer process would thus have to be extremely fast. However, such a mechanism cannot be ruled out completely. The electromagnetic fields created around GNPs upon incident illumination are strong [35], and thus some interaction leading to the excitation of the phthalocyanines after the photoexcitation of GNPs could take place.

The selective excitation of phthalocyanines was not fully possible, but anyhow, at the excitation wavelength of 680 nm mainly phthalocyanines are absorbing. GNP solution and phthalocyanine solutions were used as reference samples. The phthalocyanine toluene solution is not the perfect reference sample, because it fails to take into account the interactions between the closely packed phthalocyanines on the GNP surface. In practice, a reference sample containing inactive particles with similar packing density of phthalocyanines on the surface as in the GNPs, would be quite difficult to prepare. The component spectra of the phthalocyanine-functionalized GNPs show three components (Fig. 5B). By comparing these to the reference sample spectra, it was possible to make the following conclusions: the longest-living component has a lifetime and shape similar to the phthalocyanine reference and can be attributed to those phthalocyanines that are not quenched. The two shorter-living components have both features from GNPs and phthalocyanines, but an important new feature is a photoinduced absorption band around 840–1000 nm. This looks very similar to a phthalocyanine radical cation band observed in films of phthalocyanine-fullerene dyads [36].

Recently, a study on bis(diarylamino)biphenyl-functionalized GNPs indicated charge transfer or exciton creation between chromophores that are closely packed on the GNP surface [37]. In the case of

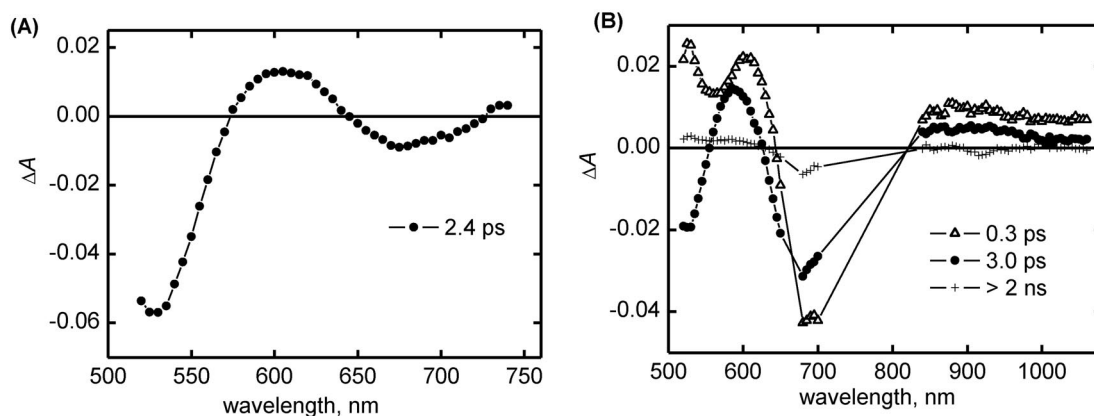


Fig. 5 Decay component spectra obtained from global fitting of pump–probe data for phthalocyanine-functionalized GNPs: (A) excitation of mainly gold cores at wavelength of 500 nm and (B) excitation of mainly phthalocyanines at wavelength of 680 nm. Reprinted in part with permission from *J. Phys. Chem. C* **114**, 162 (2010). Copyright © 2010 American Chemical Society.

phthalocyanine-functionalized GNPs, there is only radical cation band observed and no indication of a phthalocyanine radical anion band. It is possible that the radical anion band is not resolved, but on the other hand this could also indicate electron transfer from the phthalocyanines to the gold cores. The charges recombine fast, which is different from studies on pyrene-functionalized GNPs, where the charge recombination takes place in microseconds [5].

CONCLUSIONS AND OUTLOOK

The photoinduced processes in chromophore–GNP assemblies are various and can be controlled, for example, by the choice of the chromophore, excitation wavelength, distance between the chromophore from the GNP surface and in general by the assembly of the system. This shows that GNPs can be considered as versatile building blocks for photoactive devices. However, in order to use them, it is important to study and understand their interactions with chromophores in detail. Especially the charge-transfer processes require further studies in order to find out in detail the effect of, for example, solvent polarity, GNP size, length and type of linkers and packing density of the chromophores on the charge separation and recombination. Considering photoactive devices, which most likely will use materials in solid form, it was important to show that thin film preparation can yield nearly as strong interactions as covalent attachment. This is clearly a benefit also considering studies on interaction mechanisms, because thin film preparation is in a way much easier compared to preparation of functionalized GNPs.

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